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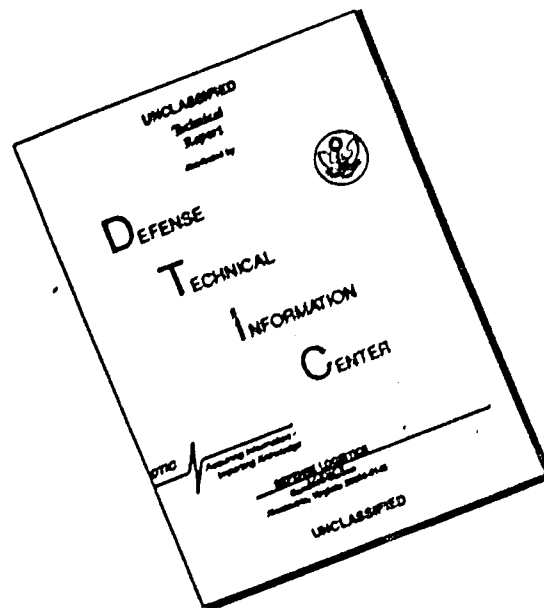
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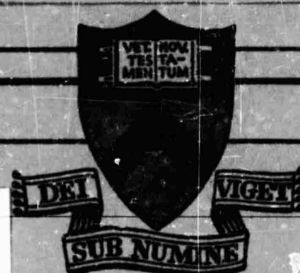
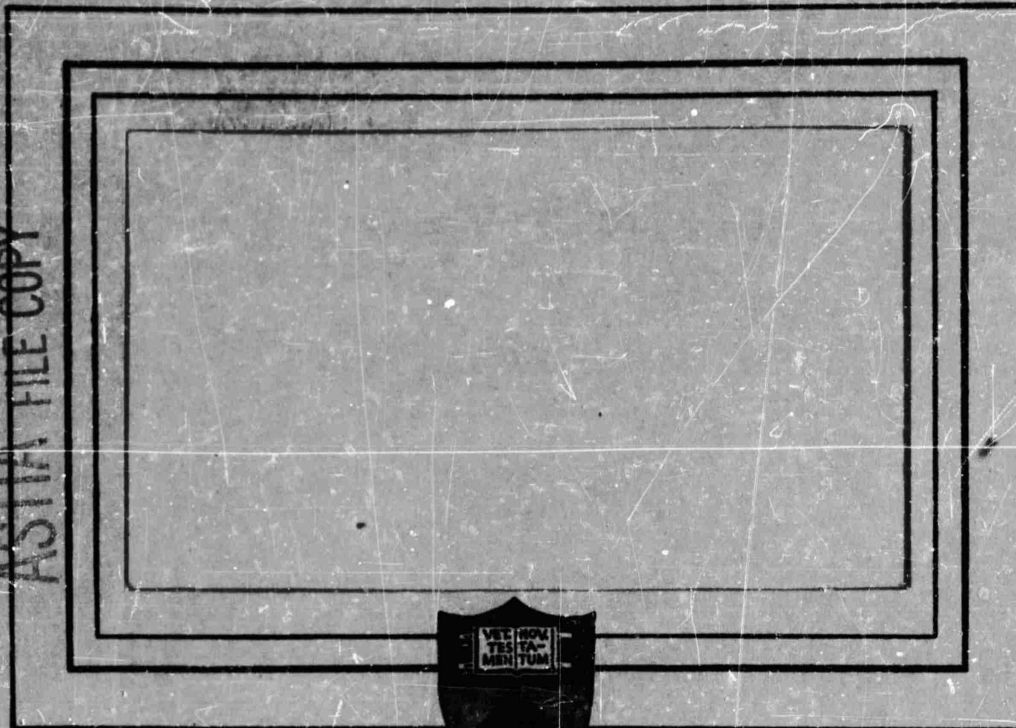
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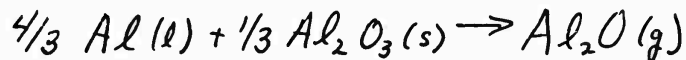
PRINCETON UNIVERSITY
DEPARTMENT OF AERONAUTICAL ENGINEERING

Addenda and Errata
to
METAL COMBUSTION PROCESSES

by
Irvin Glassman

ARS Preprint No. 938-59
AFOSR T.N. No. 59-1043
Princeton University Aero Eng'g Lab Report No. 473

- Pg 6, line 17 After the word "oxidizer" insert "at the flame front".
line 18 After the word "oxidizer" insert "at the front".
line 24 After the word "flames" insert the following sentence.
"The fact that the oxide condenses simplifies the
diffusion equations generally used in droplet analyses."
line 24 Insert the word "the" before "metal".
line 26 Change last word to "Thus".
Pg 7, line 2 Insert word "curve" after "distribution".
line 19 After "metals" insert "or metallized solid propellant".
Pg 8, line 19 After the number "1100°K" insert the following sentence
in parenthesis "(At this temperature the vapor specie
above a B-B2O3 mixture is more correctly written as the
complex molecule B2O2 (93))".
Pg 9, line 14ff Change stoichiometry of the equation to



The paragraph following should read: "Farber lists the value of ΔH_f° (25°C) for $Al_2O(g)$ as -34 kcal/mole. Since the ΔH_f° of $Al_2O_3(s)$ is -399 kcal/mole, the above reaction is highly endothermic and thus limits the temperature. Since BO has a ΔH_f° of only -5.3 kcal/mole a similar situation exists for boron. It is obvious for metal oxides which decompose into elemental metal vapor, metal suboxides and/or oxygen atoms."

- Pg 10, line 6 After end of sentence insert the following sentence.
"A list of the major species for the vaporization of metal oxides under various conditions is given at the end of Ref. 93."
- line 17 Insert "adiabatic" before "temperature".
- line 18 Insert "in oxygen" after "aluminum".
- Pg 12, line 10 Insert "and physics" after "chemistry".
- Pg 14, line 10 Insert "burning" before "droplet".
- line 15 Last word should read "partial".
- line 23 After "coefficient" add "relative to the metal".
- Pg 15, line 11 Should read ".....reduces to a more simplified equation....." instead of ".....to the equation.....".
- Pg 17, line 14 Should read ".....pressure of the oxygen present, that is $P_{O_2,C}$ " instead of ".....that is $P_{O_2,B}$ ".
- line 17 Change "of" to "on".
- line 20 Change "good" to "valid".
- Pg 18, line 17 Insert "generally" before "is".
- line 19 Should read ".....should have flame fronts close to....." instead of ".....should be close to.....".
- last line Insert the following sentence. "In fact, if one assumes that the thermal conductivity of the metal vapors are approximately the same, as a rough approximation, one could postulate that in the initial burning phases that the separation distances between the flame front and the metal surface for aluminum and sodium flames are relatively of the same order; that beryllium flames have a separation distance a factor of 4 less than that of aluminum; lithium a factor of 2 less; magnesium a factor of 3 greater."

Pg 19, Table III

Heading of Column 7 should read " T_M^V ". Add a column 12, with heading and values as follows:

Element	$\frac{T_{MO}^V - T_M^V}{H}$
Be	0.08
Li	0.16
Al	0.34
Mg	1.14
Na	0.32
C_6H_6	27.0

Pg 20, Paragraph 4 At the end of paragraph 4 add the reference letter (k).

last line Add "initially" after "but".

Pg 23, line 18 Change "alkylated compounds" to "liquid alkylated metal compounds".

Pg 24, line 2 Change that part of the sentence beginning "less oxide deposition....." to "less oxide deposition may or may not be a great oversimplification, for nucleation products appear to be of the order (l,m) of 0.1 to 1μ in diameter and the particles must diffuse a distance of the order of 100 to 1000 particle diameters."

Add the following references:

- k. Glassman, I., "The Stability of Propellants and the Theory of Thermal Ignition", Princeton University Aero Eng'g Lab Report No. 460, AFOSR TN 59-586, ASTIA AD No. 217 185, May, 1959.
- l. Setze, P. C., "Liquid Boric Oxide Particle Growth Rates in a Gas Stream from a Simulated Jet Engine Combustion Chamber", NACA EM 55I 20a, April 30, 1957.
- m. Schreier, S., "The Effect of a Condensed Exhaust Phase on Rocket Performance", M.S.E. Thesis in Aero Eng'g, Princeton University, 1956.

Add the following to the bibliography:

- 93. Inghram, M. G., and Drowart, J., "Mass Spectroscopy Applied to High Temperature Chemistry", Advance Papers of an International Symposium on High Temperature Technology, Asilomar, Calif., Oct. 6-9, 1959, arranged by Stanford Research Institute, Menlo Park, Calif. This manuscript contains 137 references, many of which are pertinent to metal combustion phenomena.

94. Kingery, W. D., "Oxides for High Temperature Applications", *ibid.*
95. Ackermann, R. J., and Thorn, R. J., "Reactions Yielding Volatile Oxides at High Temperatures", XVI Congrès International de Chimie Pure et Appliquée, Paris, 1957.

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A Technical Report on Contract AF 18(600)-1527

METAL COMBUSTION PROCESSES

by
Irvin Glassman

37 T

Aeronautical Engineering Laboratory Report No. 473

August 1959

Department of Aeronautical Engineering
PRINCETON UNIVERSITY
Princeton, New Jersey

ABSTRACT

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Since the light metallic elements undoubtedly will play a greater and greater role as propellants in advanced chemical and nuclear-chemical propulsion systems, interest in their burning characteristic is increasing.

~~Presented here are~~ some preliminary conclusions on burning characteristics ^{presented}

These conclusions are based on fundamental physical considerations and not on experimental results. An analytical approach to calculate the burning rate of metals is also suggested. This approach differs from the diffusion-droplet approach in that it includes radiation feed-back and loss terms. Such terms can be important at the high temperatures of the diffusion film surrounding a burning metal.

The verification of many of the postulates given in this report can be carried out ideally at some later date on the high pressure double rocket motor flow reactor developed under the subject contract.

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METAL COMBUSTION PROCESSES¹

Irvin Glassman²
Princeton University, Princeton, New Jersey

I. INTRODUCTION

Interest in artificial light sources for photography and metallic dust explosions stimulated early work on the combustion of metals. Recent endeavors to obtain higher performance with rocket motors (a)³ and ram engines (b) have led many propellant engineers to formulations which contain certain metallic elements in some form. The addition of aluminum powders to solid propellant combinations has given high specific impulse and better operating characteristics (a). However, aluminum is not necessarily the only metallic element of interest to the propulsion engineer. An interesting presentation of which substances may be best as propellants has been given by Carpenter (c) and is shown in Figure 1. In this figure there is plotted the heat of combustion in Btu per pound of fuel and oxidizer versus the atomic number. Since the flame temperature is related to the heat of combustion and in rocket motors both fuel and oxidizer must be carried, this plot gives some idea as to the relative effectiveness as propellants of various elements and compounds formed from these elements. Of course, the molecular weight of the products of combustion is important, as well, and this consideration must be taken in account. Although this graph is based upon oxygen as the oxidizer, the relative order would not be effected too greatly by selection of another oxidizer. One should note that most compounds will give a heat of combustion

1. The author's work in combustion is supported by the United States Air Force Office of Scientific Research of the Air Research and Development Command under Contract AF 18(600)-1527.

2. Associate Professor, Department of Aeronautical Engineering; Member, A.R.S.

3. Lower case letters appearing in parentheses refer to articles listed in the references at the end of this manuscript; numbers appearing in parenthesis refer to articles appearing in the bibliography which follows the references.

between the points representing the elements from which they are constituted. Immediately, one can see for propellant considerations what compounds containing elements with atomic numbers greater than 14 are of no concern, for such compounds could not compete with gasoline, and their products of combustion undoubtedly would have high molecular weights. The prominence of certain of the metallic elements as propellants is accentuated by a plot of this type and the fact that many have a higher heat of combustion than hydrogen is not generally realized. It appears that the use of the elements, or compounds containing lithium, boron, beryllium, aluminum, magnesium, and silicon as propellant additives could be most attractive. However, although these propellants will give high flame temperatures, their burning rate and other physical characteristics must be such that the efficiency and operating characteristics of the propulsive device are not impaired.

Figure 2, also taken from Carpenter (c) makes a similar comparison for air breathing engines in which the heat of combustion in Btu per pound of fuel is most important. From this figure likely fuels could be formulated from slurries of the elements, or compounds containing boron, aluminum, and magnesium. Much of the same considerations discussed above hold here as well.

A relative rating of various compounds based on the heat of combustion per pound of fuel and per pound of fuel and oxidizer is given in Table I. Hydrogen which has the highest heat of combustion per pound of fuel ranks sixth when compared on the basis of Btu per pound of fuel and oxidizer. However, the molecular weight of the products of hydrogen rocket combinations is low compared to the effective molecular weight of the products of the other substances and thus hydrogen fares much better on a specific impulse comparison. Actually Table I simply specifies which metals would be most likely as additives to hydrogen and other CHN fuels. In conventional systems metals themselves as fuels would give prohibitively high molecular weight

TABLE I
HEATS OF COMBUSTION OF VARIOUS SUBSTANCES IN OXYGEN

	<u>Fuel</u>	<u>Product</u>	<u>Btu/lb fuel</u>	<u>Fuel</u>	<u>Btu/lb</u> <u>(fuel + oxygen)</u>
1.	H ₂	H ₂ O (l)	61,000	Be	10,550
2.	Be	BeO	29,400	Li	8,640
3.	B	B ₂ O ₃	25,400	B	7,900
4.	CH ₄	CO ₂ , H ₂ O (l)	24,000	Al	7,080
5.	C ₂ H ₂	CO ₂ , H ₂ O (l)	21,400	Mg	7,000
6.	Li	Li ₂ O	18,500	H ₂	6,780
7.	C	CO ₂	14,100	Si	6,300
8.	Si	SiO ₂	13,500	C ₂ H ₂	5,250
9.	Al	Al ₂ O ₃	13,400	CH ₄	4,800
10.	Mg	MgO	11,600	Ti	4,550
11.	Ti	Ti ₂ O ₃	6,820	C	3,840

products, most of which would condense in the nozzle. However, gains in performance can be obtained with the addition of the metallic elements and thus increased attention should be given to the combustion of metals and related processes.

Undoubtedly metals added to solid propellants are consumed by diffusion flames. It can be postulated, and more will be said about this subject later, that the flames surrounding the burning metal particles represent temperatures much greater than the equilibrium adiabatic combustion temperature of the complete propellant formulation. Equilibration must take place after condensation of the metallic oxide and in later flow stages of the motor chamber. Metals added by liquid slurries should follow the same pattern.

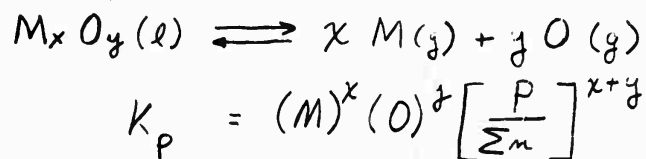
Compounds containing metallic elements may reach a more complete oxidized state by one of two procedures. The compound can be attacked and oxidized in the same way as a hydrocarbon, or the compound may decompose into the metallic element and chemical fragments. The metal particles formed then burn as diffusion flames. In all likelihood, most, but certainly not all, alkylated metal compounds or polymers will follow the latter procedure. Those compounds oxidized in the same manner as ordinary hydrocarbons are not of interest here; however, those which lead to metal diffusion flames are.

II. THE METAL DIFFUSION FLAME

The combustion of solid materials can be divided into two categories--the metals and the non-metals. The non-metals include for the most part carbon and the solid hydrocarbons and there are no great distinguishing features that make the combustion of these materials any different from the combustion of liquids. In fact, the categories could be better defined to distinguish between those materials whose combustion products have very low

boiling points and those which have high boiling points. The metals have the high boiling point metallic oxide as their products and thus have flames which exhibit certain unique or distinguishing features. A liquid such as an alkylated metal compound would fall in the same category as the pure metal since this liquid would have a high boiling oxide as a product. The temperatures that can be obtained with the combustion of metals appear to be limited to the vaporization temperature of the metallic oxide product, whether the oxide decomposes on vaporization or not. This conclusion is reached since the heats of vaporization or decomposition of the oxide are equal to the heat of reaction of the metal and oxidizer at the vaporization temperature. Eventually when the products of a metal flame diffuse to a cooler zone they condense.

Of course, the vaporization and condensation temperature varies with the pressure, and for those compounds which decompose the temperature which can be reached will also be a function of the oxygen concentration. Thus, one should judge the temperature reached from the equilibrium process which represents the vaporization dissociation process, i.e.



where M represents any metallic element, $\sum n$ is the total number of gaseous moles, and P is the total pressure. One sees that as the pressure rises and the oxygen (or oxygen atom since whichever exists is correct for the argument here) concentration rises the reaction must shift to the left. More liquid thus is present and therefore higher temperature can prevail before the liquid will decompose.

Diffusion flames of ordinary liquids or solids generally are described by the double film picture (d), as depicted in Figure 3. Heat diffuses from the flame front B to the particle surface A. The fuel vaporizes

or sublimates and diffuses from the surface A to the flame front B. Oxygen diffuses from some position C (which can be taken at infinity for a stagnant atmosphere), toward the front B. It is assumed that no reaction takes place until fuel and oxidizer reach B, that they meet here in stoichiometric portions and that the reaction takes place infinitely fast in an infinitely thin layer. Obviously, the infinite reaction rate concept cannot be a true one, but analyses developed from this picture have been successful in predicting many characteristics of liquid diffusion flames, including the burning rate of the fuel (e). More complex analyses (f) which include finite reaction kinetics, but ignore inflammability limit considerations, do not too greatly alter the basic picture, and in fact, predict the same burning rates as the simplified approach.

Generally there are then some distinctive differences which must be considered between a metal diffusion flame and those flames having only gaseous products. In the metal flame the temperature at the front is known and, as defined previously, taken as the vaporization temperature of the metal oxide. However, as will be shown later, the partial pressure of the oxidizer is not known. In the ordinary liquid diffusion flame, the partial pressure of the oxidizer is specified since the basic assumption is that the fuel and oxidizer meet in stoichiometric proportion and as a consequence the flame temperature at the front must be calculated.

The second distinction of the metal diffusion flame is that a condensable oxide is formed. As mentioned earlier the formation of the oxide really establishes the basic difference between metal diffusion flames considered here and other liquid or solid diffusion flames.

There is, however, another characteristic of metal flame which is worth noting and which may be very important. Generally the temperature in pure metal combustion is so high that there is ionization in the front. So there exists in the flame front a complex of ions, electrons, and neutral

species (60). This complex produces a high emissivity in the ultra violet (69). Since the peak of Planck's radiant energy distribution shifts to the ultra violet for these high temperatures, the emissive radiant energy of such a flame is very high. In most considerations of diffusion flames it is the heat which is conducted back from the flame through the fuel vapor which raises the temperature of the droplet to the vaporization temperature, vaporizes the fuel, and heats the vapor. It would appear then with high emissivities and high temperatures (particularly at high pressures which cause high oxide vaporization temperature) that radiant energy processes in metal flames could play an important role in determining the metal burning rate. The reflectivity of the molten metal surface receiver could then be of import and in fact it is possible that the surface condition of the burning metal could play an important part in determining its burning rate. There can be, of course, a radiant energy loss as well, and in fact (if the metal is burning in an infinite medium which acts as a black body receiver) this loss can be greater than the amount radiated to the metal surface. For metal-lized solid propellants burning in an internal burning grain, there would be no radiant energy loss since the energy would be radiated back to the propellant. For metals strands, however, burning in strand bombs, there would be a definite radiant energy loss.

Now that the distinction between metal diffusion flames and liquid droplet flames has been made, certain physical characteristics of metal combustion will be examined.

III. THE METAL FLAME TEMPERATURE

Brewer (2) reports that under highly oxidizing conditions to almost neutral conditions the metal oxide molecule (represented as M_xO_y) is the main vaporizing species for all the alkaline earth oxides except BeO , which decom-

poses to the elements upon vaporization. SrO and BaO are more important than the elements even under neutral conditions and under reducing conditions all the alkaline earth oxides vaporize predominately to the metal atom vapor. From the description of the diffusion flames given earlier, it was pointed out that for analysis purposes the fuel and oxidizer merge in some proportion and react in a definite front. More realistically, the two begin to react prior to reaching the analytically prescribed proportions and do react whenever a ratio of fuel vapor to oxidizer suitable for reaction has been reached. The largest majority of the metal then is reacting under reducing conditions. Since the metal oxide which is formed would decompose to the elements as suggested by Brewer (2), higher concentrations of oxygen would be found which further prevents the diffusion of oxygen to the reaction zone. Thus, it appears that the reaction of metal vapors in diffusion flames will be under reducing conditions and the product oxide formed will decompose upon vaporization. Decomposition upon vaporization then limits the flame temperature to the vaporization temperature of the oxide.

For boron, Brewer (2) shows that from the spectroscopic dissociation energy of BO that B_2O_3 cannot vaporize as BO . However under reducing conditions B_2O_3 will vaporize as BO . For example, a mixture of B and B_2O_3 should produce a 1 atmosphere partial pressure of BO at 1100°K . BO is stable enough that even the most stable oxides can be reduced by boron under vacuum conditions. However, the $\text{B} - \text{B}_2\text{O}_3$ condition is that which exists in elemental boron diffusion flames and here too evidence shows that the flame temperature must be the vaporization temperature of the oxide B_2O_3 .

Brewer and Searcy (1a) investigated the $\text{Al} - \text{Al}_2\text{O}_3$ system in an effusion cell. From the vapor pressure measurements they obtained a boiling point of $3800^\circ \pm 200^\circ\text{K}$ for Al_2O_3 . Farber (26) reports that their evidence for this dissociation of Al_2O_3 to Al_2O and AlO at high temperature has been substantiated by others. Al_2O is the product in a reducing atmosphere and AlO in an oxidizing atmosphere. From thermodynamic calculations, Farber was able

to show that near the boiling point the decomposition of Al_2O_3 is very considerable. Here too then is the limiting vaporization temperature effect. Farber also showed thermodynamically the extent of decomposition of Al_2O_3 under various atmospheres and conditions which can exist in propellant flames. In the presence of CO and H_2 , Al_2O_3 starts to dissociate appreciably at temperatures about 3000°K.

However, the author believes that these reactions with CO and H_2 are only of import in later stages of propellant flames when the aluminum particles have burned already as diffusion flames. The diffusion of CO and H_2 to the burning metal particle will not be as great, of course, as the diffusion of oxygen. Small equilibrium concentrations of those species will be built up through the complete diffusion flame zone. More likely the important reducing reaction would be



Farber lists the value of ΔH_f° (25°C) for $\text{Al}_2\text{O}(g)$ as -34 kcal/mole. Since the ΔH_f° of oxygen atoms is 59 kcal/mole the decomposition-vaporization reaction consumes about all the energy of formation of the Al_2O_3 and the temperature must be limited as much. Since BO has a ΔH_f° of only -5.3 kcal/mole the same situation exists for boron. It is obvious for metal oxides which decompose into elemental metal vapor and oxygen atoms.

Thus, until evidence is put forth to the contrary, it appears safe to establish the vaporization temperature of the metal vapor oxide as the adiabatic flame temperature in a metal diffusion flame for large groups of metals. The groups which fall in this category are:

- (a) Alkali metals, which include Na, K, Rb, and Cs. Li which is also in this group may have a stable gaseous oxide. However, this is yet to be determined positively.
- (b) Alkaline earth metals, which include Be, Mg, Ca, Sn, and Ba.

(c) Boron-aluminum group which includes B, Al, Sc, Y, and La.

Gaseous sub-oxides exist for these groups.

(d) Titanium - zirconium

(e) Manganese

(f) Iron group, which includes Fe, Co, and Ni.

(g) Zinc group, which includes Cd also.

(h) Silicon

As more data appear, each metal-oxygen system must be evaluated independently. Table II taken from Grosse and Conway (42) lists properties of the metals and metal oxides and the melting and boiling points. Consequently, the boiling point temperature of the oxide may be taken as the combustion temperature.

The dissociation reactions which limit temperatures obtainable are all affected by the pressure. Naturally, as the pressure is raised the dissociated products will reassociate as given by the Le Chatelier's principle. Examination of the equilibrium constants for the vaporization dissociation step readily shows that the vaporization temperature increases with an increase in pressure. It is estimated that at 1000 psia the temperature of burning aluminum would be about 5900°K.

IV. BURNING CHARACTERISTICS

With the establishment of the criterion that the boiling point of metal oxide is the metal flame temperature, certain other conclusions as to the character of the metal diffusion flame may be drawn. These conclusions are based on certain physical properties of the metals themselves.

If the vaporization temperature of the oxide is greater than the vaporization temperature of the pure metals, then the structure of the diffusion flame would be much like the double film concept applied to liquids. However, if the vaporization temperature of the pure metal is greater than

TABLE II
NORMAL MELTING AND BOILING POINTS OF METALS AND THEIR HIGHER OXIDES*

Element	Element Melting Point, $T_M^{\circ K}$	Element Boiling Point, $T_V^{\circ K}$	Oxide	ΔH_f° oxide kcal/mole	Oxide Melting Point $T_{MO}^{\circ K}$	Oxide Boiling Point $T_{VO}^{\circ K}$
Li	460	1640	Li_2O	-146.6	2000	2600
B	2570	2820	B_2O_3	-305.4	720	2520
Na	370	1150	Na_2O	- 99.4	1193	1550
Mg	920	1370	MgO	-143.7	3075	3350
Al	930	2720	Al_2O_3	-400.2	2323	3800
K	330	1030	K_2O	- 86.4	800	1750
Ca	1120	1960	CaO	-151.7	2860	3800
Ti	2000	3530	Ti_2O_3	-363.0	2400	3300
Zr	2120	5770	ZrO_2	-261.8	2960	4570
Be	1550	3240	BeO	-143.7	2820	4530
Si	1700	2870	SiO_2	-210.2	2000	2500

* Considering the basic uncertainties in the thermodynamic and physical data at high temperatures, the author wishes to point out that the data presented throughout this paper are the best he could find in today's literature. Since most data were used for relative comparisons, no effort was made to give statistical deviations from the values reported. Such deviations in many cases can be large.

the vaporization temperature of the oxide, then reaction cannot take place in the vapor phase but must take place on the molten surface at some temperature lower than the vaporization temperature of the metal but about that of the vaporization temperature of the oxide. The approach used to calculate the case when $T_{MO}^V > T_M^V$ is somewhat similar to that used for liquids and the distinctions between the two were discussed in the previous section. From Table II, it is found that Li, Na, Mg, Al, Ca, K, Be, and Si fall into this group.

When $T_M^V > T_{MO}^V$ then the oxide accumulates on the molten metal surface. The procedure for calculating the burning rate in this case becomes much more complex. The rate may be determined by the surface chemistry or by the diffusion rate of the oxidizer through a solid oxide film. B, Ti, and Zr fall into this group. The character of the film can be different according to the physical properties of the oxide. If the oxide has a lower density than the molten metal, then it will float on the surface and oxygen must reach the raw metal by crevices or openings formed due to oxide running off the surface, cracking due to expansion of the liquid, etc. However, if the oxide is lighter than the molten metal, but soluble in the metal, then some metal would always appear on the surface. If the oxide is more dense than molten metal, it would sink through the molten surface and keep a metal surface exposed to the oxidizer. Physical intuition would suggest perhaps that the burning rates of the metals would fall generally in categories according to the descriptions given above; i.e., those metals whose oxides are heavier than the molten metal would be the fastest; those which are lighter and soluble, next; and those which are lighter but not soluble, the slowest. Further metals which fall in the case $T_{MO}^V > T_M^V$ should burn faster than those in which $T_M^V > T_{MO}^V$. Thus, under the same conditions Al and Mg should exhibit faster burning rates than B, Ti, or Zr. Because the physical picture of metals in which $T_{MO}^V > T_M^V$ is the only clear one, analytical determination of the burning rates of this group alone will be treated here.

The first analytical attempt to determine the burning rate of metals taking into consideration that the oxide vaporization temperature establishes the flame front temperature was due to Coffin (77). Coffin, however, neglected the possibility of radiant heat transfer processes. The calculation of burning rates, when radiation is included, is extremely difficult. Nevertheless, the form of the resulting expressions can indicate the importance of various physical and chemical parameters. Given below is the development of Coffin and Brokaw (37) for the burning of magnesium; this development is modified to take into account radiation effects.

Coffin replaces the flame front of infinitesimal thickness used in the regular double film concept by a high temperature zone of diffusion and reaction at the boiling point of the oxide. Pictorially this model is reported in Figure 4 and could be thought of as three films. MgO condenses outside the high temperature zone and it is assumed that this product cannot diffuse toward the droplet.

The high temperature zone BB' is one of constant temperature. The oxygen concentration is zero at B and some unknown value of B'. Inside the zone MgO can exist and dissociate to the elements. At B', MgO condenses completely.

In the AB region, there is not net flow of any component except fuel. Products are assumed to pass outward. The energy equation in zone AB is then

$$W_f [\Delta H + L^v + H_{Mg} - H_{Mg,A}] = 4\pi X^2 k_{AB} \frac{dT}{dx} + R_G \quad (1)$$

where W_f = fuel mass transfer rate, moles/sec

ΔH = sensible heat of fuel to the boiling point, cal/mole

L^v = latent heat of vaporization, cal/mole

H = enthalpy, including chemical energy, cal/mole

X = radius from center of particle, cm.

k = thermal conductivity, cal/cm sec $^{\circ}\text{C}$

T = temperature, $^{\circ}\text{C}$ or $^{\circ}\text{K}$

R_G = a radiant energy term

The only difference between this equation and that of Coffin and Brokaw is the term R_G . R_G is a function of the emissivities (ϵ_A , ϵ_B) and the absorbing characteristics of the Mg vapor in AB. For a droplet system the area S at A and at B enter in the radiation term, however, in a strand burning along the cylindrical axis Equation 1 would be developed by a one-dimensional approach and the area cancels throughout all equations.

For a droplet, though, and particularly for most metals, $S_B - S_A$ is so small that $S_B \approx S_A$ and thus the solution of the final equations is simplified. The actual conditions in BB' are such that $\epsilon_B \approx 1$, as discussed in Section II. ϵ_A is affected by the reflectivity of the surface, and if the molten surface is highly reflective ϵ_A could be of the order of a tenth. Nevertheless $T_B^4 - T_A^4$ is so large, at high values of pressure and oxygen particle pressure that it would appear the radiation term still could not be neglected. Thus, the physical condition of the surface of molten metal can be of some importance in determining its burning rate.

In the region B', oxygen diffuses inward, and the MgO floats out. The energy equation in this zone is

$$W_s [Q + m_{O_2} (H_{O_2} - H_{O_2,C}) - m_{MgO} (H_{MgO} - H_{MgO,C})] = 4\pi r_{B'C}^2 \frac{dT}{dx} + R_L \quad (2)$$

where Q = heat of combustion at reference temperature, cal/mole

n = stoichiometric coefficient

R_L = a radiant energy term

R_L is a term which enters only in droplet or strand burning tests and is a radiation loss to the surrounding.*

* The introduction of the terms R_G and R_L is similar to the suggestion of Summerfield (g) that such terms should be introduced in determining the burning rates of composite propellants.

Coffin and Brokaw do not include this R_L term either. If the particles are burning in an internal burning solid propellant grain, the energy is transmitted back to the grain and is not lost. Since most basic experiments are performed with spheres or strands, this term should be included when comparisons are made between experiment and theory. Since the energy is accepted by an infinite absorbing atmosphere or cold walls, R_L can be written, then, as

$$R_L = \sigma S_A T_B^4 \quad (3)$$

where σ is the Stefan-Boltzmann constant. Again for this term it is assumed that $S_B \approx S_B \approx S_A$.

Because of the condensed product, the diffusion equation for oxygen generally used for other systems reduces to the equation for the diffusion of oxygen through a stagnant film of ambient inert gas

$$\frac{W_{O_2}}{4\pi x^2} = - \frac{D_{O_2} P}{RT(P-p_{O_2})} \frac{dp_{O_2}}{dx} \quad (4)$$

where D = diffusion coefficient, sq cm/sec

P = total pressure, atm

p = partial pressure, atm

R = universal gas constant

The diffusion equation for oxygen and the energy equation for the outer zone B'C, combined and integrated, is

$$\frac{D_{O_2}}{n_{O_2} RT k_{B'C}} \int_{p_{O_2,C}}^{P_{O_2,B'}} \frac{P}{P-p_{O_2}} dp_{O_2} = \int_{T_C}^{T_{B'}=T_{B,P}} \frac{dT}{[Q + m_{O_2}(H_{O_2} - H_{O_2,C}) - m_{mgo}(H_{mgo} - H_{mgo,C}) - \frac{R_L}{W_f}]}$$

In the high temperature zone BB' the energy equation as written

by Coffin is

$$W_{m_g} H_{m_g} + W_{O_2} H_{O_2} + W_{mgo} H_{mgo} - W_f H_{f_0} = 0 \quad (6)$$

and the continuity for each species is

$$2W_{O_2} + W_{MgO} = 0 \quad (7)$$

$$W_{Mg} + W_{MgO} = W_f \quad (8)$$

Combining with the energy equation

$$W_{Mg}(H_{f_0} - H_{Mg}) - 2W_{O_2}(H_{MgO} - H_{f_0} - \frac{1}{2}H_{O_2}) = 0$$

$$W_{Mg} = -2W_{O_2} \left(\frac{H_{MgO} - H_{f_0} - \frac{1}{2}H_{O_2}}{\Delta H + L' + H_{Mg} - H_{Mg,A}} \right)$$

$$W_{Mg} = -2\theta W_{O_2} \quad (9)$$

$H_{MgO} - H_{f_0} - \frac{1}{2}H_{O_2}$ equals the heat of combustion of Mg at T_0 to form condensed MgO at the boiling point for the given conditions. Then

$$W_f = -2(\theta+1)W_{O_2} \quad (10)$$

At atmospheric pressure θ for magnesium equals about two. It may be regarded as the ratio of the amounts of MgO condensed at the outer and inner boundaries of the BB' zone.

With substitution of the above equation into the diffusion equations

one has

$$\frac{W_f}{4\pi x^2} = \frac{D_{O_2} P (2\theta+1)}{RT [P + (2\theta-1)p_{O_2}]} \frac{dp_{O_2}}{dx} \quad (11)$$

Integrating the equations one obtains

$$\int_{x_A}^{x_B} \frac{W_f}{4\pi x^2} dx = \int_{T_A}^{T_{B'}} \frac{k_{AB}}{[H_{Mg} - H_{f_0} - \frac{R\theta}{N_f}]} dT = \alpha \quad (12)$$

$$\int_{x_B}^{x_{B'}} \frac{W_f}{4\pi x^2} dx = \int_{p_{O_2}=0}^{p_{O_2,B'}} \frac{D_{O_2} P (2\theta+2)}{RT [P + (2\theta-1)p_{O_2}]} dp_{O_2} = \beta \quad (13)$$

$$= \frac{D_{O_2} P (2\theta+2)}{RT (2\theta-1)} \ln \frac{P + (2\theta-1)p_{O_2,B'}}{P} = \beta$$

$$\int_{x_B}^{x_C} \frac{W_f}{4\pi x^2} dx = \int_{T_B}^{T_C} \frac{dT}{[Q + m_{O_2}(H_{O_2} - H_{O_2,c}) - m_{H_2O}(H_{H_2O} - H_{H_2O,c}) - \frac{R_c}{W_f}] = \delta \quad (14)$$

Combining the above three integrals

$$\int_{x_A}^{x_C} \frac{W_f}{4\pi x^2} dx = \alpha + \beta + \delta \quad (15)$$

For $\frac{1}{x_C} \rightarrow 0$

$$\frac{W_f}{4\pi x_A} = \alpha + \beta + \delta \quad (16)$$

A possible approach to the solution of the equations would be to assume a value of W_f so that the radiation terms could be calculated and then determine the W_f from the remainder of the equations. Reiterate until the value assumed is equal to the value calculated.

α , β , and δ are positive with the log term dominating, particularly in oxygen rich atmospheres. Equation 5 used for calculating P_{O_2}, δ' shows a strong dependence of P_{O_2}, δ' upon $P_{O_2,c}$. Further, it has been shown that the vaporization temperature of the metal oxide is dependent on partial pressure of the oxygen present, that is P_{O_2}, δ' . This dependence is felt strongly in the radiation term introduced where the temperature is raised to the fourth power. Thus, for metal combustion there is an even stronger dependence of burning rate of the oxygen partial pressure than there is in liquid droplet combustion.

In the above analysis it was assumed that none of the product oxide diffused toward the droplet. There is some question as to how good this assumption is for various substances. Obviously, the droplet represents a

sink for the oxide. For large droplets (i.e., long overall burning times) there could be deposition of oxide on the molten metal surface, even in the class of metals discussed here, and thus the burning rate can be hindered in the manner described for the metals which surface react. Another factor which could determine the amount of oxide that would diffuse back to the molten surface and thus hinder the burning rate, is the relative location of the burning front to the metal surface. Those metals which would have fronts closer to the surface than others would be expected to have the greatest difficulty from oxide deposition.

It can be seen from the development above that the burning rate basically is controlled by the oxygen diffusion. The temperature gradient which governs the heat flux from the flame front to molten metal then adjusts to give the proper rate. Since the flame temperature is a constant, the relative location of the front depends on the difference between the vaporization temperatures of the oxide and the metal and the heat of vaporization of the metal. The enthalpy necessary to raise metal to the vaporization temperature is small with respect to the heat of vaporization. Thus those metals for which T_{MO}^V is close to T_M^V should find the flame front close to the surface. Similarly metals with high heats of vaporization should be close to the surface also. From Table III one would expect that for aluminum where T_{MO}^V is close to T_M^V that the flame front is close to the surface, and for magnesium the flame front should be much further from the surface since T_{MO}^V is much greater than T_M^V . Similarly a lithium flame should be very close to the surface because of its high heat of vaporization.

From the above analysis it would follow then that aluminum and lithium would show more serious oxide surface deposition due to diffusion than magnesium. One could estimate this relatively from the ΔH_{TOT} data in Table III and through discussion given above.

TABLE III
HEAT CONTENT TERMS FOR VARIOUS METALS

Element	C _p Solid	M.P. T°C	Δ H Solid Cal/gm	L ^M Cal/gm	C _p liquid	BP T°C	Δ H liquid cal/gm	L ^V cal/gm	Δ H _{tot} cal/gr	T _{MO} ^V °C
Be	.50					3170	1570*	8355*	9930	4000
Li	1.10	186	177	32.8	1.1	1317	1245	4648	5100	2300
Al	.24	660	152	95.4	.26	2500	464	2260	2970	3500
Mg	.28	651	175	88.8	.33	1103	150	1337	1750	3100
Na	.28	98	20	27.2	.30	883		1005	1290	1300
C ₆ H ₆					.40	80	22	94	116	

* Based on sublimation process

V. IGNITION

The balance between a rate of heat production and the rate at which heat can be removed determines whether a substance will ignite and react (46). In the case of fuel droplets and particularly for metals, this factor is largely dependent upon how fine is the sub-division, i.e. particle size. Smaller particles have a large surface to volume ratio, and hence a higher rate of heat production per unit volume, and a lower cooling rate.

If the surface area to volume ratio is very large, the conduction of heat from the flame front by the metal particle is greatly reduced. Heat loss then is by the relatively slow heat transfer process in a gas. Thus, neighboring particles of metal reach the ignition temperature with great rapidity. If finely divided powder is loosely packed together, the heat loss by convection largely is eliminated and under such conditions of low heat loss, spontaneous ignition of metal can occur.

When solid metal rods are used, conduction by the metal rapidly absorbs large quantities of heat from the burning front, and little heat is left for raising the temperature of the adjacent metal to the ignition temperature.

Consequently, as with other combustible substances, when in bulk, metal can be made to burn at a controlled rate, whereas when divided, it will burn with great violence.

In regard to metal particles of widely different sizes flowing in a combustible stream, it would appear then that large particles will take a longer time to heat to the ignition point, and thus have longer ignition time than smaller particles. Thus, there will be a definite size effect in regard to ignition.

The character of the ignition process is entirely different from that of the combustion process in that the ignition process is most likely not a diffusion type flame, but a surface burning phenomena. The transition

pattern from a surface ignition process to a diffusion flame has not been reported. The process is most likely something as follows. The surface reacts and the temperature rises sufficiently to vaporize the metal and subsequent reaction between the hot metal vapor and oxygen proceeds as a diffusion flame. However, if during the ignition process the oxide coats the surface so that there is slow burning of the ignited metal, then radiative transfer could vaporize and ignite neighboring particles which would burn as diffusion flames. However, if the ignition sources were energetic enough to vaporize the metal initially, there is no doubt the metal would burn as a diffusion flame.

Grosse (42) reports that metals can be divided into three classes according to their ignition process. In the first class are those metals that ignite below their melting point and includes Mg, Ca, Ti, Zr, Mo, Fe, Ca; In the second class are those that ignite above their melting point and include Al, Li, and Na; and, of course, there are those metals that do not ignite, Hg, Ag, and Pt.

VI. DISCUSSION AND CONCLUSIONS

Throughout the previous sections reference was made to various practical conclusions that would be reached by the description of the metal burning process proposed here. A more detailed discussion of the various topics will be given here.

One topic of major interest worth further discussion is the temperature reached in the burning of metals. As previously stated most metals of interest in propulsion are limited to combustion temperatures which correspond to the vaporization temperature of the higher metal oxide. However, this temperature varies with the pressure or in the case of a mixture of gases with the oxygen, or oxidizer, partial pressure. In propulsion systems

when the metal is only a fuel additive, a somewhat more complex situation exists. Here there are two competing processes. One is associated with the burning of the fuel and the other with the burning of the metal. It is proposed that the metal particles burn as diffusion flames described in earlier sections of the article. If this is so, the temperature of the diffusion flame zone surrounding the burning metal particle will be dependent upon the oxygen partial pressure and this temperature will be different from the adiabatic combustion temperature of the complete propellant mixture. Except under unusual circumstances one would expect the diffusion flame temperature of the metal to be greater than the adiabatic flame temperature of the mixture. The equilibration of temperature zones must take place outside the active reaction zone. The availability of oxygen for the metal combustion in a solid propellant is difficult to predict. If the oxidizer and hydrocarbon fuel are also burning as a diffusion flame as is most likely in a composite propellant (g), then the metal should not find too great a deficiency of oxygen. Even in homogeneous propellants the various reaction states taking place would be slow enough that any metal particles added would be able to compete for oxidizer. However, one could think of many situations, such as fine metal particles added to a premixed hydrogen-oxygen gas mixture prior to entering a flame front, in which the gaseous fuel would burn with much greater rapidity than metal. The metal would thus burn in a stream depleted of oxygen and the temperature of the flame around the metal particle would be lower than if it had burned more completely in the earlier stages of the flame.

Obviously then, when the metal is an additive to a fuel or a solid propellant the situation is most complex. However, in composite solid propellant it would appear to the author that the temperature of the flame surrounding the metal particle would be much greater than the equilibrium temperature and that the possibility that radiant energy exchange is an important factor

in determining the burning rate, as suggested by Summerfield (g), is an excellent one. Of course, the higher the temperature the more pertinent the radiation term. The higher the radiation term the less sensitive should be the pressure dependency of the burning rate.

The character of the burning process of substances which contain metallic elements will vary according to the reaction procedure for complete oxidization. Consider for an example a metal which falls in the category $T_M^V > T_{MO}^V$. Such metals when added in elemental form or through a compound which decomposes to give the elemental form of the metal should have long burning times and thus could give poor combustor efficiencies. Boron is a typical example. However, if the metallic element could be added in compound form such that the compound does not decompose before oxidization, then oxidization of the compound directly could take place and the elemental burning process eliminated. Again taking boron as an example, if a boron compound could be oxidized in the same manner as an ordinary hydrocarbon where the oxygen attaches to the carbon (or boron for the example) before decomposition (h) the slower burning rate of metal burning for $T_M^V > T_{MO}^V$ is circumvented.

For the alkylated compounds which do decompose into hydrogen, hydrocarbon fragments, and the elements, then there can be stages of combustion with the hydrogen burning first, fragments next, and then the metals. As discussed above, the depletion of oxygen concentration could effect the temperature of the metal flame front and the burning rate.

Discussion in the earlier sections led to the conclusion for certain metals in the group $T_{MO}^V > T_M^V$ that the flame front will be close to the metal surface and consequently there may be oxide surface coating due to diffusion. In a composite solid propellant the flame front is less than 100μ from the surface (i) and from Table III one would expect that metal flames would be even closer to the surface. Considering this general proxi-

mity of flame front to surface, the postulate that certain metals will have less oxide deposition may be a great oversimplification. This area may be a fruitful one for experimental investigation. The author and his students are initiating such experimental investigations which will be based on burning of small diameter metal strands at high oxygen concentrations and total pressures. Pressure release during strand burning should quench the flame and permit surface examination by metallurgical photomicrography. Flame front and metal surface separation distance measurements will be attempted by optical techniques.

Other experimental investigations will include the measurement of burning rates of metal strands under various conditions in order to compare the results with the theory which was given earlier and which include the radiation terms. Relating strand rates to spherical particle rates has recently been accomplished by Mead (J). Spectroscopic examination of the various zones of the diffusion flame is anticipated and should give most important information on the metal combustion process.

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VIII. NOMENCLATURE

c_p = specific heat, cal/gm °C

D = diffusion coefficient, cm²/sec

H = enthalpy, including chemical energy, cal/mole

ΔH = sensible heat of fuel, with no subscript then to the boiling point, cal/mole

ΔH_c = heat of combustion, Btu/lb fuel or Btu/lb (fuel and oxidizer)

$\Delta H_{tot} = \Delta H_{solid} + L^M + \Delta H_{liquid} + L^V$, cal/gm

k = thermal conductivity, cal/gm cm °C

K_p = equilibrium constant

L = latent heat, cal/mole or cal/gm

n = stoichiometric coefficient

$\sum n$ = total number of moles of gases

p = partial pressure, atm

P = total pressure, atm

Q = heat of combustion at reference temperature, cal/mole

R = universal gas constant, cm³ atm/ mole

R_G, R_L = radiant energy terms

S = surface areas, cm²

T = temperature, °C or °K

W = mass transfer rate, moles/sec

X = radius from center of particle, cm

α, β, γ = integrals

ξ = emissivity

σ = Stefan-Boltzman constant

θ = heat content ratio

Subscripts

A, B, B', C = positions specified in Figures 3 and 4

f = fuel

l = liquid

M = metal

MO = metal oxide

o = reference state

Superscripts

M = melting point

V = vaporization or boiling point

IX. REFERENCES

- a. Anonymous, "Plastisol Propellant Unveiled," Chem. and Eng. News, July 27, 1959, p. 22.
- b. Olsen, W. T., and Setze, P. C., "Some Combustion Problems of High Energy Fuels for Aircraft," Seventh Combustion Symposium, Rhelnhold, New York, p. 883.
- c. Carpenter, R. A., "Liquid Rocket Propellants," Ind. and Eng. Chem., Vol. 49, (April 1957) p. 48A.
- d. "Basic Considerations in the Combustion of Hydrocarbon Fuels with Air," NACA Report 1300, p. 220.
- e. Penner, S., and Goldsmith, M., "On the Burning of Single Drops of Fuel In an Oxidizing Atmosphere," Jet Prop., Vol 24, (1954) p. 245.
- f. Lorrell, J., and Wise, H., "Burning of Liquid Droplets with Finite Reaction Kinetics, J. or Chem. Phys., April 1956.
- g. Summerfield, M., "Total Radiation from Burning Solid Propellant Strands," Project SQUID Semi-Annual Progress Report, April, 1959.
- h. Walsh, A. D., "Oxidization of Hydrocarbons," Trans. Faraday Soc., Vol. 42, (1946) p. 269.
- i. Sutherland, G., "The Mechanism of Combustion of an Ammonium Perchlorate-Polyester Resin Composite Solid Propellant," Ph.D. Thesis, Princeton University, 1956.
- j. Mead, G. A., "Relation of Droplet Consumption Rates to Liquid Strand Consumption Rates," ARS Journal, Vol. 29, (1959) p. 440.

X. BIBLIOGRAPHY*

Thermodynamic Properties (General)

1. Brewer, L. and Searcy, W., "High Temperature Chemistry," Annual Review of Physical Chemistry, Vol. 7, 1956, pp. 259-286.
- 1a. Brewer, L., and Searcy, A. W., J.A.C.S., Vol. 73, (1951), p.5308.
2. Brewer, L., "The Thermodynamic Properties of the Oxides and Their Vaporization Processes," (Chemical Review), Vol. 52, Feb. 1953, pp.1-75.
3. Coughlin, P., "Contributions to the Data on Theoretical Metallurgy, XII, Hears and Free Energies of Formation of Inorganic Oxides," Bureau of Mines, Bulletin No.542, 1954, 80 pp.
4. Erway and Seifert, "Vapor Pressure of Beryllium Oxide," J. of Electrochem. Soc., Vol. 98, (1951) p.83.
5. Glassner, A., "The Thermochemical Properties of the Oxides, Fluorides and Chlorides to 2500°K," Atomic Energy Commission, ANL-5750, 1957, 70 pp.
6. Gordon, S., "High Temperature Chemistry as Applied to Metal-Based Propellants," Jet Propulsion, Vol. 28, Nov. 1958, pp.769-770.
7. Gordon, J. S., "Thermodynamics of High-Temperature Gas Mixtures, and Application to Combustion Problems," WADC Tech. Rep. 57-33 (1957).
8. Huff, N., Gordon, S., and Morrell, V. E., "General Method and Thermodynamic Tables for Computation of Equilibrium Composition and Temperature of Chemical Reactions," NACA Report No.1037, 1951.
9. Kallman, H. K., and Krieger, F. J., "The Thermodynamic Properties of Boric Oxide and of Aluminum Oxide in the Ideal Gaseous State," Rand Corporation, Report P-120, Feb. 1, 1949.
10. Kelley, I. K., "Contributions to the Data on Theoretical Metallurgy XI Entropies of Inorganic Substances," Bureau of Mines, Bulletin No.477, 1950.
11. Kelley, K. K., "Contributions to the Data on Theoretical Metallurgy X High Temperature Heat-Content, Heat-Capacity, and Entropy Data for Inorganic Compounds," Bureau of Mines, Bulletin No.476, 1949.

* NACA reports on the physical characteristics, handling, and power plant performance of metal-fuel slurries have not been included in this bibliography. Only those reports with explicit combustion aspects are included.

12. Kelley, K. K., "Contributions to the Data on theoretical Metallurgy, III, Free Energies of Vaporization and Vapor Pressures of Inorganic Substances," Bureau of Mines, Bulletin No.383, 1935.
13. Kubaschewski, O., and Catterall, J. A., "Thermochemical Data of Alloys," New York, Pergamon Press, 1956.
14. Kubaschewski, O., and Hopkins, B. E., "Oxidation of Metals and Alloys," New York, Academic Press, 1953.
15. Latimer, W. M., "Tables of Free Energy Functions for Elements and Compounds in the Range of 2000°-5000°K," Atomic Energy Commission, MDDC-1462, Revised 1952.
16. National Bureau of Standards Report 6297, "Preliminary Report on the Thermodynamic Properties of Lithium, Beryllium, Magnesium, Aluminum and Their Compounds with Oxygen, Hydrogen, Fluorine, and Chlorine," January 1959.
17. National Bureau of Standards Report 6252, "Thermodynamic Properties of Boron and Its Compounds," December 1959.
18. Rossini, D., Wagman, D., Evans, H., Levine, S., and Jaffe, I., "Selected Values of Chemical Thermodynamic Properties," National Bureau of Standards, Circular No.500, 1952.
19. Scott, D. W., "Thermochemistry and Thermodynamic Properties of Substances," Annual Review of Physical Chemistry, Vol. 6, 1955, pp.1-24.
20. Soulen, J. R., "Vaporization of Boron Oxide and Other Group Three Oxides," (Wisconsin University, Thesis, Ph.D. 1955) Ann Arbor, Mich., University Microfilms, Inc. Publication No.16212 (Dissertation Abstracts, Vol. 16, 1956, pp.883-884).
21. Soulen, J. R., Sthapitanonda, P., and Margrave, J. L., "Vaporization of Inorganic Substances: B_2O_3 , TeO_2 and Mg_3N_2 ," Journal of Physical Chemistry, Vol. 59, Feb. 1955, pp.132-136.
22. Stull, D. R., and Sinke, G. C., "Thermodynamic Properties of the Elements," (Advances in Chemistry Series, No.18) Washington, D.C., American Chemical Society, November 1956.

Thermodynamic Properties
(Al, Be, B)

23. Cochran, C. N., J. Amer. Ceramic Soc., Vol. 77, 1955, p.2560.
24. Evans, W.H., Wagman, D. D., and Prosen, E. J., "Thermodynamic Properties of Some Boron Compounds," National Bureau of Standards Report No.4943, August 31, 1956.
25. Evans, W. H., Wagman, D. D., and Prosen, E. J., "The Vapor Pressures of Some Boron Compounds," National Bureau of Standards, Report No.6663, December 3, 1957.
26. Farber, M., "Thermodynamics of Al_2O_3 ," Jet Propulsion Vol. 28, November 1958 pp.760-762.

27. Hall, E. W., and Weber, R. J., "Tables and Charts for Thermodynamic Calculations Involving Air and Fuels Containing Boron, Carbon, Hydrogen, and Oxygen," NACA Research Memorandum E56B27, July 1956.
28. Hock, M. and Johnston, H. L., J. American Ceramic Soc., Vol. 76, 1954, p.2560.
29. Kaweck, H. C. (to Beryllium Corp.) "High-purity Beryllium Oxide," U.S. Patent No. 2,647,821, Aug. 4, 1953; Chemical Abstracts 47:11678f
30. Nathan, C. C., "The Heat of Combustion of Boron and of Lithium Borohydride," Pittsburgh University, Bulletin, Vol. 46, No.10, June 5, 1950.
31. Pack, D. H., and Hill, G. R., "Thermodynamic Data and Bond Energies for Some Boron Compounds," Utah University, Department of Chemistry Technical Report No. MCC-1023-TR-169, June 1955, 67 pp. (Final Technical Report, Contract N0a(s)-1023.) (ASTIA AD 103146)
32. Parry, R. W., Schultz, D. R., and Giradot, P. R., "The Preparation and Properties of Hexamminecobalt (III) Borohydride, Hexamminechromium (III) Borohydride and Ammonium Borohydride," American Chemical Society, Journal Vol. 80, January 11, 1958, pp.1-3.
33. Ritter, D. M., "Equilibria and Kinetics Among Substituted Diboranes," University of Washington, Seattle, Technical Report No. MCC-1023-TR-178, June 1955, 37 pp. (Final Report, Contract N0a(s)-1023.) (ASTIA AD 103443)
34. Setze, P. C., "A Review of the Physical and Thermodynamic Properties of Boric Oxide," NACA Research Memorandum E57B14, April 1957.
35. Speiser, R. Nalditch, S., and Johnston, H. L., "The Vapor Pressure of Inorganic Substances, II, B_2O_3 ," American Chemical Society, Journal, Vol. 72, June 1950, pp.2578-2580.

Metal Combustion (General)

36. Banus, M. D., and McSharry, J. J., (To Metal Hydrides, Inc.) "Increasing the Burning Rate of Metal Powders," U. S. Patent No. 2,688,575, Sept.7,1954.
37. Coffin, K. P., and Brokaw, R. S., "A General System for Calculating Burning Rates of Particles and Drops and Comparison of Calculated Rates for Carbon, Boron, Magnesium, and Iso-octane," NACA Technical Note No.3929, Feb.1957.
38. Foster, H. H., Fletcher, E. A. and Straight, D. M., "Aluminum Borohydride-Hydrocarbon Mixtures as a Source of Ignition for a Turbojet Combustor," NACA Research Memorandum E54K12, February 1955.
39. Fletcher, E. A., Foster, H. H. and Straight, D. M., "Aluminum Borohydride as an Ignition Source for Turbojet Combustor," NACA Research Memorandum E53G15, September 1953.
40. Gibbs, J. B. and Cook, P. N., Jr., "Preparation and Physical Properties of Metal Slurry Fuels," NACA Research memorandum E52A23, March 1952.

41. Godbert, A. L., and Would, L. O., "Flammability of Magnesium, Aluminum, and Magnesium Aluminum Alloy Dusts," Great Britain, Safety in Mines Research Establishment, Research Report No.113, 1955.
42. Grosse, A. V., and Conway, J. B., "Combustion of Metals in Oxygen," Industrial and Engineering Chemistry, Vol. 50, April 1958, pp.663-672.
43. Grosse, A. V., and Conway, J. B., "Office of Naval Research High Temperature Project," Final Report, Temple University, Research Institute July 1, 1954.
44. Grosse, A. V., "The Production of High Temperature by Chemical Means and Particularly by the Combustion of Metals," Stanford Research Institute and the University of California, High Temperature - a Tool for the Future, Proceedings of the Symposium, Berkley, California, June 25-27, 1956, Menlo Park, California, Stanford Research Institute, 1956, pp.59-68.
45. Gulbransen, E. A., "Kinetic and Structural Factors Involved in Oxidation of Metals," Industrial and Engineering Chemistry, Vol. 41, July 1949, pp.1385-1391.
46. Harrison, P. L., "Combustion of Titanium and Zirconium," Seventh Combustion Symposium, Rheinhold, New York, 1959, p.931.
47. Hartmann, I., "Recent Research on the Explosibility of Dust Dispersions" Industrial and Engineering Chemistry, Vol. 40, April 1948, pp.752-758.
48. Hartmann, I., Nagy, J. and Jacobson, M., "Explosive Characteristics of Titanium, Zirconium, Thorium, Uranium, and Their Hydrides," Bureau of Mines, Reports of Investigations, No.4835, December 1951.
49. Hartmann, I., Nagy, J. and Brown, H. R., "Inflammability and Explosibility of Metal Powders," Bureau of Mines, Reports of Investigations No.3722, October 1943, 44 pp.
50. Liempt, J. A. M. van, and Vriend, J. A. de, "Light from the Combustion of Some Metals," Receuil Travaux Chimiques du Pays-Bas, Vol. 56, 1937, pp.126-128.
51. Liempt, J. A. M. van, and Vriend, J. A. de, "The Light of Combustion of Aluminum-Zinc and Aluminum-Cadmium Alloys," IBID, Vol. 56, 1937, pp.594-598.
52. Liempt, J. A. M. van, and Vriend, J. A. de, "The Light of Combustion of Some Metals and Alloys," IBID, Vol. 58, 1939, pp.423-432.
53. Lord, Albert M., "An Experimental Investigation of the Combustion Properties of a Hydrocarbon Fuel and Several Magnesium and Boron Slurries," NACA Research Memorandum E52B01, April 1952.
54. Marsel, J., and Kramer, L., "Spontaneous Ignition Properties of Metal Alkyls," Seventh Combustion Symposium, Rheinhold, New York, 1959, p.906.
55. Reynolds, W. C., "An Investigation of the Ignition Temperature of Solid Metals," Summary Report, Stanford University, Department of Mechanical Engineering, June 1957.

55a. Spalding, D.C., "Some Fundamentals of Combustion," Academic Press, New York, (1955) p.118.

56. Titman, H., and Wynn, A. H. A., "The Ignition of Explosive Gaseous Mixtures by Friction," Revue de l'Industrie Minérale, Vol. 36, 1955,

Metal Combustion
(Li and Si)

57. Downie, A. R., and Barrow, R. F., "Silicon Flame Bands," Nature, London, Vol. 160, August 9, 1947, p.198.

58. Smit, J. A., and Vendrik, A. J. H., "Ionization of Metal Vapors in a Flame," Physics, Vol. 14, 1948, pp.505-509.

Metal Combustion (Al)

59. Badin, E. J., "Oxidation of Metal Alkyls and Related Compounds," Symposium on Combustion, Flame and Explosion Phenomena, 3rd, Baltimore, Williams and Wilkins Co., 1949, pp.386-389.

60. Brockman, F. G., "The Nature of the Light Emitter in Photoflash Lamps," Optical Society of America, Journal, Vol. 37, August 1947, pp.652-659.

61. Cassel, H. M., Liebman, I., and Mock, W. K., "Radiative Transfer in Dust Flames," Symposium (International) on Combustion, 6th, New York, Rheinhold Publishing Corp. 1957, pp.602-605.

62. Cassel, H. M., Das Gupta, A. J., and Guruswamy, S., "Factors Affecting Flame Propagation Through Dust Clouds," Symposium on Combustion, Flame and Explosion Phenomena, 3rd, Baltimore, Williams and Wilkins Co., 1949, pp.185-190.

63. Chesterman, W. D., "The Photographic Study of Rapid Events," Oxford, Clarendon Press, 1951, p.47.

64. Cueilleron, J. and Scartazzini, H., "Combustion of Aluminum in Oxygen," Comptes Rendus, Vol. 228, 1949, pp.489-490.

65. Forsythe, W. E., and Easley, M. A., "Characteristics of the General Electric Photoflash Lamp," Optical Society of American, Journal, Vol. 21, October 1931, pp.685-689.

66. Forsythe, W. E., and Easley, M. A., J. Optical Society, Vol. 24, p.195 (1934).

67. Liempt, J. A. M. van, and Vriend, J. A. de, "Aluminum and Aluminum-Magnesium Light," Receuil des Travaux Chimiques du Pays-Bas, Vol. 54 1935, pp.239-244.

68. Liempt, J. A. M. van, and Vriend, J. A. de, Philips Tech. Rev., Vol. 1, p.289 (1936).

69. Salin, R. de, "Combustion of Aluminum in Air," Comptes Rendus, Vol.234 1952, pp.2437-2439.

70. Tominaga, H., "Combustion of Aluminum Powder," Chemical Society of Japan, Journal, (Industrial Chemistry Section), Vol. 53, 1950, pp.106-108.
71. Wartenberg, H. Von, "Alumina," Zeitschrift fur anorganische und allgemeine Chemie, Vol. 269, 1952, pp.76-85.

Metal Combustion (B)

72. Experiment, Inc., "Combustion of Elemental Boron," Quarterly Summary Reports, 1956-1958.
73. McDonald, G. E., "Thermal Decomposition of Ethylpentaborane in Gas Phase," NACA Research Memorandum E56D26, July 1956.
74. Porter, R. F., and Dows, D. A., "Blue Emission from the Vapor of Burning Boron," Journal of Chemical Physics, Vol. 24, pp.1270-1271.

Metal Combustion (Mg)

75. Bulewicz and Sugden, "Determination of the Dissociation Constants and Heats of Formation of Molecules by Flame Photometry Part Stability of MgO and MgOH," Trans. Faraday Society, Vol. 55, May 1959, p.720.
76. Cook, P. N., Jr., Evans, V. E., and Lezberg, E. A., "Experimental Investigation of Physical and Combustion Properties of Several Residual Fuel Oils and Magnesium - Fuel-Oil Slurries in a Ram-Jet-Type Combustor," NACA Research Memorandum E53D30, June 1953. *AD-13613*
77. Coffin, K. P., "Burning Times of Magnesium Ribbons in Various Atmospheres," NACA Technical Note No.3332, December 1954.
78. Coffin, K. P., "Some Physical Aspects of the Combustion of Magnesium Ribbons," Symposium (International) on Combustion, 5th, New York, Rheinhold Publishing Corp., 1955, pp.267-276.
79. Fassell, W. M., Jr., Gulbransen, L. B., Lewis, J. R., and Hamilton, J. H., "Ignition Temperatures of Magnesium and Magnesium Alloys," Journal of Metals, Vol. 3, July 1951, pp.522-528, (Transactions Section).
80. Keil, A., "Spectrochemical Investigation on the Beryllium Effect in Magnesium Alloys," Zeitschrift fur Metallkunde, Vol. 42, 1951, pp.13-16.
81. Leontis, T. E., and Pashak, J. F., (to Dow Chemical Co.), "Fiberizing Magnesium," U.S. Patent No. 2,656,796, Nov. 3, 1953. Chemical Abstracts Vol. 48:1932h (1954).
82. Lord, A. M. and Evans, V. E., "Effect of Particle Size and Stabilizing Aditives on the Combustion Properties of Magnesium Slurry," NACA Research Memorandum E52K12, January 1953. *AD-1427*
83. Scartazzini, H., "Combustion of Magnesium Powder in Oxygen," Comptes Rendus, Vol. 230, January 1950, pp.97-98.

84. Terem, H. N., "Sur La Cinetique de l'oxydation du magnesium," Comptes Rendus, Vol. 226, March 1948, pp.905-906.
85. Veits, I. V., Gurvich, L. V., and Korobov, V. V., "Determination of the Dissociation Energy of Metal Oxides (Sr, Ca and Mg) by Measuring the Intensity of Resonance Lines of Metal Atoms in Flame Spectra," Akademi Nauk SSSR, Izvestia, Ser. Fiz., Vol. 19, No.5-6, 1955, pp.21-22.

Experimental Techniques

86. Allen, H., Jr. and Tannenbaum, "A Method for the Analysis of Compounds Containing Boron, Carbon, and Hydrogen," NACA Research Memorandum E54L15, March 1955. *AD-56121*
87. Andersen, H. C., and Belz, L. H., "Burning Time and Ignition-Temperature Apparatus for Metal Powders," Review of Scientific Instruments, Vol. 24, 1953, p.1004.
88. Conference on Extremely High Temperatures, Boston, Mass., March 18-19, 1958, Sponsored by Air Force Cambridge Research Center, New York, John Wiley & Sons 1958.
89. Leo, W., "Determination of the Color Temperature of Photoflash Lamps," Zeitschrift fur angewandte Photographie in Wissenschaft und Technik, Vol. 4, 1942, pp.3-6.
90. Line, L., Jr., Clark, W. J., and Rahman, J. C., "An Apparatus for Studying the Burning of Dust Clouds," Symposium (International) on Combustion, 6th, New York, Rheinhold Publishing Corp., 1957, pp.779-786.
91. Wolfhard, H. G., and Parker, W. G., "Temperature Measurements of Flames Containing Incandescent Particles," Physical Society, London, Proceedings, Vol. B62, Part 8, August 1, 1949, pp.523-529.
92. Wolfhard, H. G., and Parker, W. G., "Emissivity of Small Particles in Flames," Nature, Vol. 162, August 1948, pp.259.

XI. LIST OF FIGURES

- Figure 1 Heat of Combustion in Btu per pound of fuel and oxidizer vs atomic number of principal elements, from Carpenter (C).
- Figure 2 Heat of combustion in Btu per pound of fuel vs atomic number of principal elements, from Carpenter (C).
- Figure 3 Cross-sectional model of burning fuel particle, from Coffin and Brokaw (37).
- Figure 4 Cross-sectional model of burning fuel particle having high boiling point exhaust product, from Coffin and Brokaw (37).

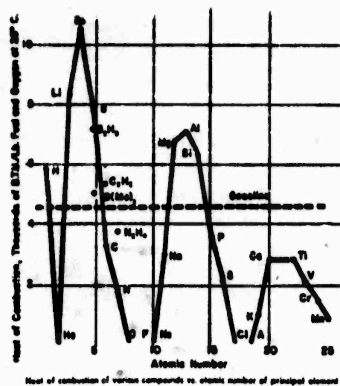


FIGURE 1

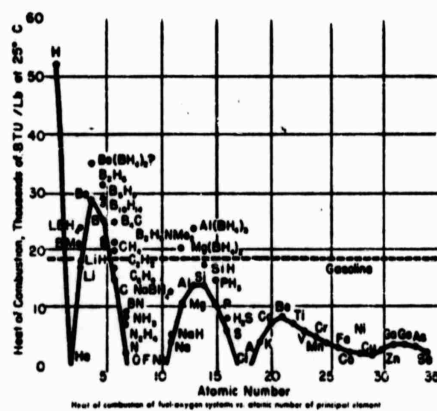


FIGURE 2

